

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Appl. No. : 10/828,530 Confirmation No. 4322  
Applicant : Laszlo J. Kecskes et al  
Filed : April 6, 2004  
TC/AU : 1742  
Examiner : George P. Wyszomierski  
Docket No. : ARL 03-60  
Customer No. : 37064

Commissioner for Patents  
P.O. Box 1450  
Alexandria VA 22313-1450

**DECLARATION UNDER 37 C.F.R. § 1.132**

I, Laszlo J. Kecskes, having been advised of the penalties for perjury under 18 U.S.C. § 1001, state as follows:

1. I was awarded a Ph.D. in 1996 in Materials Science and Engineering by the University of Delaware.
2. I was awarded a M.S. in Physics by the University of Minnesota in 1985 & a B.S. in Physics in 1981 by Rensselaer Polytechnic Institute.
3. I have been employed by the U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Ordnance Materials Team located at the Aberdeen Proving Ground Maryland since February 1985. I was Acting Team Leader of the Ordnance Materials Team from February 2005 until September 2006.
4. I have numerous publications and presentations such as the following:  
*Refereed Journal Papers:* Single Author: 4; Primary Author: 14; Contributing Author: 24  
*Symposium Publications:* Single Author: 5; Primary Author: 18; Contributing Author: 35

*Government Documents:* Single Author: 4; Primary Author: 10; Contributing Author: 9

*Other Publications:* Single Author: 2; Primary Author: 2; Contributing Author: 3

*Invited Presentations to/Invited Appearances before Professional Groups:* 4

*Professional Societies, Associations, and Universities:* 59

*Other Presentations (within DOD):* 63

5. I have read the Office Action mailed 21 July 2008 and understand the Examiner to be saying that Claims 1-6, 9, 11-15, 28, 30, 31, & 34-40 are considered unpatentable over Gu *et al.* J. of Non-Crystalline Solids.

6. I understand the Examiner's position is that if "x" in the formula of Gu is equal to approximately 0.8, then an alloy according to the instant claims would be produced."

7. The intent of Gu *et al.* is to systematically study the effect of enriching a Zr-based metallic glass alloy, i.e., Vitreloy 105 ( $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ ), with substituting Hf for Zr, demonstrating the extreme difficulty of forming a good glass forming alloy. Although, a reverse dilution of a Hf-based alloy is possible with Zr, the intent of the Applicants, in contrast to that of Gu, is to rely on Gu's data to produce a purely Hf-based metallic glass alloy without the presence of Zr. Vitreloy 105 has an excellent glass forming ability, as demonstrated by a wide undercooled region, low liquidus temperature, high reduced glass transition temperature,  $T_{rg}$ , and a limited number of crystalline species upon devitrification.

8. The intent of Gu is to produce a series of higher-density metallic alloys starting with a good glass forming Zr-based alloy, Vitreloy 105 and system atically enriching it with Hf to increase the overall alloy density. Although the density is found to increase, Gu finds that the substitution of Hf leads to unexpected degradation of glass forming ability. The reference makes several key observations:

it is difficult to form a good glass forming alloy based on direct Hf substitution for Zr.

the glass forming ability monotonically decreases, as measured by the reduced glass transition temperature; and

the number of crystallization peaks (species) increase from one to three as the amount of Zr is decremented to 0.

These effects are attributed to the affinity of Zr and Hf for the other alloy components. The simultaneous competition for Cu, Ni, Al, and Ti by both Zr and Hf creates more confusion in the crystallization kinetics, however, not in a beneficial manner. It is further explained that the

nucleation kinetics and subsequent growth of species are different in the Zr- and Hf-based systems, respectively. No further explanation is offered in the reference.

9. The Applicants have been familiar with the work of Gu; see acknowledgements in the reference. Unlike Gu, Applicants have postulated that the observed differences are attributed to different locations of the respective eutectics, or lowest melting point compounds, for the Zr-Cu-Ni and Hf-Cu-Ni ternary subsets. The eutectic location in the Hf-Cu-Ni system is non-obvious from that of the Zr-Cu-Ni system. Whereas, the Zr-Cu-Ni eutectic is roughly at  $Zr_{67}Cu_{17}Ni_{16}$ , the Hf-Cu-Ni 'eutectic' is at  $Hf_{53}Cu_{30}Ni_{15}$ .

10. As shown in Figure 1, this is demonstrated from an existing phase assessment for the former and from experimental data generated by the Applicants for the latter.

11. The intent of the Applicants is to produce a metallic glass alloy based on Hf only. While Claim 1 implies the presence of more than five components, unless the ratio of Cu:Ni is fixed per Claims 7 and 8, similar results are obtained as those of Gu.

12. Adjustment of the value of x to about 0.8 to 0.85 will result in a metallic glass that has poor glass forming ability. This is demonstrated by Applicants' data, shown in Figures 2 and 3, wherein Gu's results are reproduced. The ratios of glass transition temperature to liquidus are lower, but within the same data set, they are consistent with Gu's data. The  $T_{rg}$  values cannot be directly related to Gu's, most likely Gu used purer elemental constituent than did the Applicants.

13. The Applicants demonstrate their effort on improving the glass forming ability of a Hf-based metallic glass. As shown in Table 1, within the Hf-based alloy series, as indicated by  $T_{rg}$ , a small deviation from the ideal composition leads to a rapid degradation of glass forming ability. The novelty of the Applicants invention is the single exotherm and narrow solidus to liquidus transition exhibited by the ideal composition, as contrasted to the multiple number of exotherms and wider solidus-to-liquidus transition of the Hf equivalent of Vitreloy 105. See Figures 4 and 5.

14. Applicants invention is clearly differentiated from that of Gu.

APPENDIX:

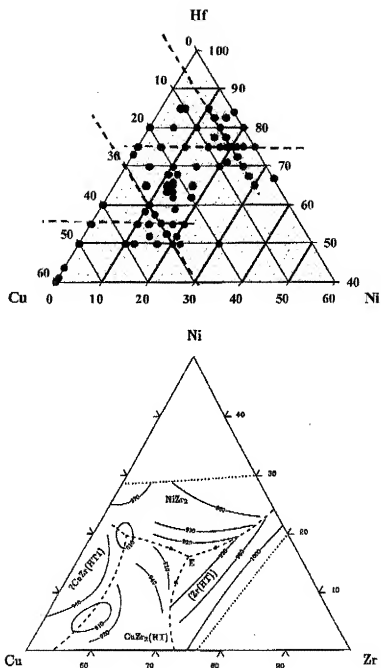


Figure 1. Locus of all experimentally fabricated alloys in Hf-Cu-Ni ternary composition space and the location of the eutectic (E) in the Zr-Cu-Ni system.

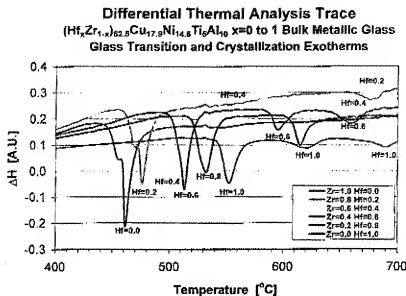


Figure 2. Crystallization events in the Hf-substituted Vitreloy 105 composition series, showing the increasing number of exotherms with decreasing Zr content.

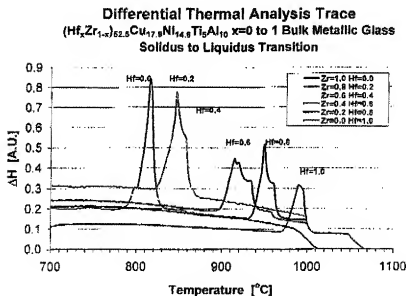
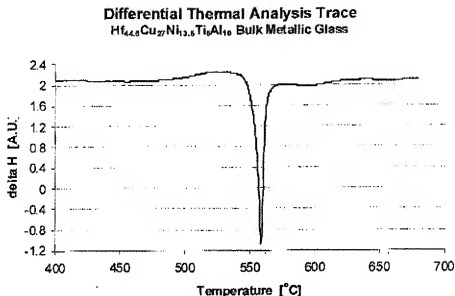


Figure 3. Solidus to liquidus transition in the Hf-substituted Vitreloy 105 composition series, showing the increasing differential melting of multiple crystalline species in each alloy as exemplified in the increase of the width of transition.

Table 1. Deviations from the ideal composition and their effect on  $T_g$ .

| Ingot#  | Rod #      | Composition (atomic %)          | Liquidus (°C) | T <sub>g</sub> onset (°C) | T <sub>g</sub> |
|---------|------------|---------------------------------|---------------|---------------------------|----------------|
| 20503-6 |            | Hf47 Cu26 Ni13 Al10 Ti5         | 985           |                           |                |
|         | 020503-6SC |                                 |               | 483                       | 0.601          |
| 21203   |            | Hf44.5 Cu27 Ni13.5 Al10 Ti5     | 983           |                           |                |
|         | 21203-4    |                                 |               | 499                       | 0.615          |
| 21903-3 |            | Hf46.75 Cu25.5 Ni12.75 Al10 Ti5 | 986<br>1024   |                           |                |
|         | 21903-3-2  |                                 |               | 485                       | 0.602<br>0.584 |
| 21903-2 |            | Hf44.5 Cu27 Ni13.5 Al10 Ti5     | 984           |                           |                |
|         | 21903-2-1  |                                 |               | 494                       | 0.610          |
| 42103-1 |            | Hf49 Cu24 Ni12 Al10 Nb5         | 1042          |                           |                |
|         | 42103-1-1  |                                 |               | 501                       | 0.589          |
| 42103-2 |            | Hf44.5 Cu27 Ni13.5 Al10 Nb5     | 1036          |                           |                |
|         | 42103-2-1  |                                 |               | 507                       | 0.596          |
| 61003-1 |            | Hf44.5 Cu29 Ni11.5 Al10 Ti5     | 1024          |                           |                |
|         | 61003-2-1  |                                 |               | 497                       | 0.594          |
| 61003-1 |            | Hf44.5 Cu25 Ni15.5 Al10 Ti5     | 987           |                           |                |
|         | 61003-1-2  |                                 |               | 488                       | 0.604          |
| 62003-1 |            | Hf46.5 Cu27 Ni11.5 Al10 Ti5     | 1005          | (observed)                |                |
|         | 62003-1-2  |                                 |               | 481                       | 0.590          |
| 62003-2 |            | Hf42.5 Cu27 Ni15.5 Al10 Ti5     | 1038          |                           |                |
|         |            |                                 | 1040          | (observed)                |                |
|         |            |                                 |               | 513                       | 0.599          |
| 62403-1 |            | Hf46.5 Cu25 Ni13.5 Al10 Ti5     | 987           |                           |                |
|         | 62403-1-1  |                                 |               | 501                       | 0.614          |
|         |            |                                 |               | 496                       | 0.610          |
|         |            |                                 |               | 498                       | 0.612          |
| 62403-2 |            | Hf42.5 Cu29 Ni13.5 Al10 Ti5     | 1013          | (observed)                |                |
|         | 62403-2-1  |                                 |               | 519                       | 0.616          |
| 80103-2 |            | Hf38.5 Ti5 Nb5 Cu27 Ni13.5 Al10 |               | No T <sub>g</sub>         |                |

(a)



(b)

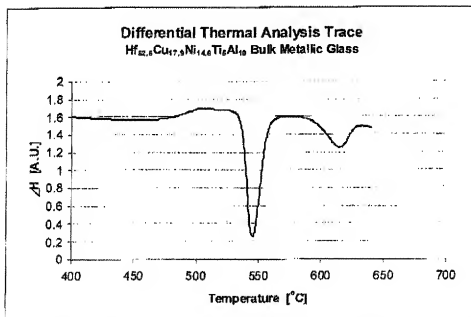
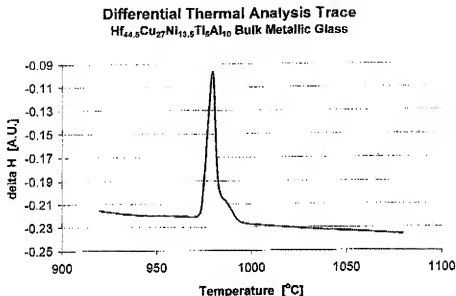


Figure 4. (a) crystallization event of the alloy claimed in the invention, showing a single exotherm. (b) crystallization events of the fully substituted Vitreloy 105 alloy, showing the first two exotherms. The third exotherm was omitted for convenience.

(a)



(b)

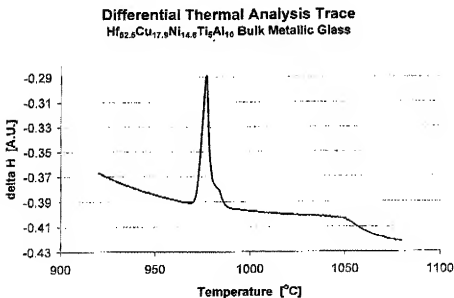
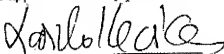


Figure 5. (a) solidus to liquidus transition of the alloy claimed in the invention, showing a narrow endotherm. (b) solidus to liquidus transition of the fully substituted Vitreloy 105 alloy, showing a significantly wider endotherm.

15. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

A handwritten signature in dark ink, appearing to read 'Laszlo J. Kecskes', written over a horizontal line.

Laszlo J. Kecskes, Ph.D.